

of the reversible $E_{1/2}$ of the $\text{FeL}^{2+} + e^- \rightarrow \text{FeL}^+$ step is taken as the potential midway between the peak potentials of the cathodic and anodic peaks. This $E_{1/2}$ value falls on the appropriate line in Figure 4.

A linear dependence of $E_{1/2}$ on IP was also reported recently for a series of metalloporphyrins and metallophthalocyanines.¹⁶ The linear relationship was observed for the oxidation step, $\text{M(II)} - e^- \rightarrow \text{M(III)}$, with the metals Ni, Co, and Fe when the third ionization potentials of the metals were used. It is interesting that with the cyclic amines the linear relationship holds for Cu, Ni, and Co but does not extend to Fe. The $E_{1/2}$ for Fe(II) occurs 1.2 V more positive than predicted from the IP. The reason for the failure of Fe(II) to fit the linear relationship is not clear but it is probably due to the participation of a different set of orbitals in the oxidation process of lower energy than those involved

(16) A. Woldberg and J. Manassen, *J. Amer. Chem. Soc.*, **92**, 2982 (1970).

with the Cu, Ni, and Co complexes. In a reversible oxidation process an electron is extracted from the highest occupied orbital and $E_{1/2}$ is related to the energy of this orbital. In an octahedral environment (both Co(II) and Fe(II) crystallize with axially coordinated acetonitrile) low-spin Co(II) has one electron in the higher energy e_g set of orbitals. This set of orbitals is empty for Fe(II) and an electron must be extracted from the lower energy t_{2g} orbitals. This would cause a positive shift in the $E_{1/2}$ vs. IP line as observed. In support of this argument is the observation that the linear relationship does extend to Fe for the $\text{M(I)} - e^- \rightarrow \text{M(II)}$ step which would be expected since Fe(I) has an electron in the e_g orbitals. Since the metalloporphyrins and metallophenalocyanins probably maintain essentially a square-planar geometry in the solvents in which the electrochemical measurements were carried out, a discontinuity in the linear $E_{1/2}$ vs. IP relationship would not be expected at Fe(II) for these complexes.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF IOWA, IOWA CITY, IOWA 52240

The Oxidation of Hexaaquoiron(II) by Chlorine(III) in Aqueous Solution

By MARTIN G. ONDRUS AND GILBERT GORDON*

Received August 27, 1971

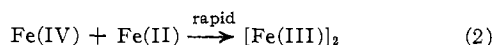
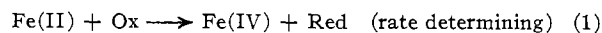
The oxidation of iron(II) by chlorine(III) appears to occur *via* a one-electron-transfer mechanism. The reaction was studied at 10 and 25° under pseudo-first-order conditions with iron(II) being in excess. Chloride ion and phenol were added to the reaction mixtures in order effectively to eliminate complicating side reactions of the intermediate product chlorine(I). The reaction rates are essentially unaffected by chloride ion concentration. The hydrogen ion dependence is appropriate to the rate expression

$$-\frac{d[\text{Fe(II)}]}{dt} = k_1[\text{Fe(II)}][\text{Cl(III)}] + \frac{k_2[\text{Fe(II)}][\text{Cl(III)}]}{[\text{H}^+]}$$

At 25° and 2.0 M ionic strength, $k_1 = (1.89 \pm 0.09) \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$ and $k_2 = 58 \pm 10 \text{ sec}^{-1}$. The results are discussed in terms of several possible one-electron-transfer mechanisms.

Introduction

Conocchioli, Hamilton, and Sutin¹ have studied the oxidation of iron(II) by a number of possible two-electron oxidizing agents. They observed that hypochlorous acid and ozone react with iron(II) to produce appreciable amounts of the iron(III) dimer, $[\text{Fe(OH)}_2\text{-Fe}]^{4+}$. The overall second-order kinetics are consistent with the dimer being formed according to eq 1 and 2.



Those reactions in which little or no dimer is produced are assumed to proceed primarily *via* a one-electron pathway.

Chlorine(III) is known to react with tris(1,10-phenanthroline)iron(II) by a mechanism which is dependent on the dissociation of the complex prior to the oxidation step.² In view of the fact that this reaction also ap-

pears to involve a two-electron-transfer process, it is of interest to make comparisons with other analogous iron(II) reactions.

In the present study of the iron(II)-chlorine(III) reaction, we have attempted to differentiate between one- and two-electron-transfer mechanisms by a detailed evaluation of the rate law and by observing the formation of the iron(III) dimer.

Experimental Section

Chemicals.—Stock solutions of iron(II) perchlorate were prepared by dissolving reagent grade iron wire in 1 M perchloric acid with gentle heating to increase the rate of dissolution. Iron(II) solutions were stored at 5° and handled under a nitrogen atmosphere by using syringe techniques to transfer the solution. The concentration of iron(II) solutions was determined by titration with primary standard potassium dichromate.

Phenol was purified by fractional distillation at 20 mm.³ Solutions were prepared gravimetrically by diluting the purified solid to the appropriate volume.

Lithium perchlorate was prepared from the reaction of the carbonate with perchloric acid and was twice recrystallized from water. Stock solutions were adjusted to pH 7 in order that the

(1) T. J. Conocchioli, E. J. Hamilton, and N. Sutin, *J. Amer. Chem. Soc.*, **87**, 926 (1965).

(2) B. Z. Shakhshiri and G. Gordon, *ibid.*, **91**, 1103 (1969); M. Ondrus and G. Gordon, *Inorg. Chem.*, **10**, 474 (1971).

(3) E. B. Grimley, Ph.D. Thesis, University of Iowa, Iowa City, Iowa, 1971.

rate of chlorine(III) disproportionation would be slow in solutions which contain sodium chlorite and lithium perchlorate.

Distilled water passed through Barnsted inorganic and organic purification columns was used throughout.

Analytical grade sodium chlorite was obtained from Matheson Coleman and Bell and was analyzed according to the following techniques. The per cent sodium chloride was determined by Mohr titration.^{4,5} The per cent sodium hypochlorite was determined iodometrically⁵ and spectrophotometrically⁶ at pH 9 in the presence of sodium borate buffer. Sodium chlorite was determined iodometrically in 0.2 *M* sulfuric acid. The per cent chlorate was calculated from the total oxidizing power in 6 *M* hydrochloric acid which had been deaerated by adding sodium bicarbonate.⁵ Analysis of the solid yielded 98.8% sodium chlorite, 0.23% sodium hypochlorite, 0.26% sodium chloride, and 0.79% sodium chlorate. Chlorine(III) solutions for kinetic experiments were prepared gravimetrically and the concentrations were verified iodometrically.

All other chemicals were reagent grade and were used without further purification.

Procedures.—The appearance of the iron(III) dimer and its subsequent decomposition at 25°, in the absence of added chloride ion or phenol, were monitored at 340 nm on a Durrum-Gibson stopped-flow spectrophotometer. The amount of dimer produced was determined by assuming a molar absorptivity⁷ of $3.0 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$. Per cent yields were calculated on the basis of a theoretical yield of 1 mol of dimer for every mole of chlorine(III) present initially.

The stoichiometry of the iron(II)-chlorine(III) reaction was determined on a Cary 14 recording spectrophotometer and on a Durrum-Gibson stopped-flow spectrophotometer. The stoichiometry is defined according to the equation

$$\text{stoichiometric ratio} = \frac{\text{moles of Fe(II) consumed}}{\text{moles of Cl(III) consumed}} \quad (3)$$

In all experiments, chlorine(III) was the limiting reagent. The stoichiometric ratio was calculated from the initial chlorine(III) concentration and from the concentration of iron(III) produced. Measurements both in the presence and in the absence of chloride ion were carried out at 240 nm where the molar absorptivity⁸ of iron(III) is $4160 \text{ M}^{-1} \text{ cm}^{-1}$. At 240 nm, iron(III) and monochloroiron(III) appear to exhibit an isosbestic point. However, the absorbance of 10^{-4} M iron(III) solutions in 1.0 *M* perchloric acid is about 5% greater than in 1.0 *M* hydrochloric acid due to the formation of di- and trichloroiron(III) complexes.

Kinetic experiments were carried out under pseudo-first-order conditions with iron(II) being in great excess. The progress of the reaction was followed at 240 nm on a Durrum-Gibson stopped-flow spectrophotometer. Although iron(III) is the primary absorbing species, chlorine(III)^{9,10} and phenol do contribute to the overall absorbance. At 240 nm, $\log \epsilon_{\text{phenol}} = 1.7$, $\log \epsilon_{\text{HClO}_2} = 2.2$, and $\log \epsilon_{\text{ClO}_2^-} = 1.7$.

Solutions for the reaction kinetics were prepared on the same day that the experiments were carried out. Sodium chlorite solutions contained 2.00 *M* lithium perchlorate and, in all but the initial experiments, 4×10^{-4} to $12 \times 10^{-4} \text{ M}$ phenol. Iron(II) solutions included the appropriate concentrations of hydrochloric acid, perchloric acid, and/or lithium chloride. The ionic strength was adjusted to 2.00 *M* when necessary with lithium perchlorate. The drive syringes and reaction chamber of the stopped-flow instrument were thermostated to $\pm 0.05^\circ$.

Results

The Iron(III) Dimer.—A number of experiments at 25° and various hydrogen ion concentrations showed evidence for the production of small quantities of the iron(III) dimer, $[\text{Fe}(\text{OH})_2\text{Fe}]^{4+}$. To bring about a measurable absorbance change at 340 nm, it was necessary to use higher concentrations of chlorine(III) than

that used in most kinetic experiments. The highest per cent yields were measured at low hydrogen ion concentrations because the decomposition of the dimer is acid catalyzed.¹ In each stoichiometric experiment, the total concentration of this product was estimated by extrapolating the disappearance curve to a zero-time transmittance. Table I illustrates that dimer produc-

TABLE I
PER CENT YIELD OF IRON(III) DIMER IN THE REACTION OF IRON(II) WITH CHLORINE(III) IN THE ABSENCE OF INITIALLY ADDED CHLORIDE ION OR PHENOL^a

$10^4[\text{Cl(III)}],$ <i>M</i>	$10^3[\text{Fe(II)}],$ <i>M</i>	Obsd abs ^d	% yield
0.512	7.68	0.010	3.3
2.18 ^b	5.76	0.026	2.0
2.18 ^c	5.76	0.046	3.5

^a In 0.17 *M* H^+ with $\mu = 2.00 \text{ M}$ at 25°. ^b In 0.96 *M* H^+ . ^c In 0.13 *M* H^+ . ^d The predicted absorbance is based on a theoretical dimer concentration equal to the initial chlorine(III) concentration. At 340 nm, $\epsilon_{\text{dimer}} (3.0 \pm 1.0) \times 10^3 \text{ cm}^{-1} \text{ M}^{-1}$; light path 2.00 cm.

tion under all conditions is less than 5% of the theoretical yield.

Reaction Stoichiometry.—In the absence of an effective scavenger, the stoichiometry of the iron(II)-chlorine(III) reaction varies. However, at high iron(II) concentrations, the $[\text{Fe(III)}]_{\text{produced}}/[\text{Cl(III)}]_{\text{consumed}}$ ratio approaches 4.0 as shown in Table II. The addition of either phenol or chloride ion

TABLE II
THE STOICHIOMETRY OF THE IRON(II)-CHLORINE(III) REACTION IN THE ABSENCE OF PHENOL AND CHLORIDE ION

$10^3[\text{Cl(III)}],$ <i>M</i>	$10^3[\text{Fe(II)}],$ <i>M</i>	$[\text{Fe(III)}]_{\text{produced}}/$ $[\text{Cl(III)}]_{\text{consumed}}$
3.28	0.48	3.35 ^a
3.28	0.96	3.44 ^a
2.56	1.92	3.29 ^b
5.0	2.50	3.41 ^c
5.0	4.90	3.75 ^c

^a Stopped-flow absorbance measurement at 10° and 0.5 *M* H^+ . ^b Same measurements at 25°. ^c Cary 14 absorbance measurement at 25° and 1.0 *M* H^+ .

to reaction mixtures reduces the stoichiometric ratio to about 2.5 under the conditions recorded in the first two rows of Table III. The presence of both chloride

TABLE III
THE EFFECT OF PHENOL AND CHLORIDE ION ON THE IRON(II)-CHLORINE(III) REACTION STOICHIOMETRY^a

Temp, °C	$[\text{Cl}^-], \text{ M}$	$10^4[\text{phenol}],$ <i>M</i>	$[\text{Fe(III)}]_{\text{produced}}/$ $[\text{Cl(III)}]_{\text{consumed}}^b$
25.0	0.00	4.2	2.53 ^c
25.0	0.50	0.00	2.48 ^c
25.0	0.50	4.2	1.95 ± 0.10
10.0	0.50	7.7	2.04 ± 0.10
10.0	1.00	2.0	2.06 ± 0.08
10.0	0.50	2.0	1.93 ± 0.08
10.0	0.10	2.0	1.96 ± 0.06
10.0	0.05	2.0	1.95 ± 0.06

^a Determined from stopped-flow experiments in which $[\text{Fe(II)}]_0 = 7.7 \times 10^{-4}$ to $6.7 \times 10^{-3} \text{ M}$, $[\text{Cl(III)}]_0 = 2.5 \times 10^{-5}$ or $4.93 \times 10^{-5} \text{ M}$, $[\text{H}^+] = 0.05\text{--}1.00 \text{ M}$, and $\mu = 2.00 \text{ M}$. ^b The error estimates are standard deviations from the mean for experiments at various hydrogen ion and iron(II) concentrations. ^c Only one experiment was carried out under these conditions.

ion and phenol reduces the ratio to approximately 2.0 over a fairly broad range of initial conditions.

(4) L. A. Prince, *Anal. Chem.*, **36**, 613 (1964).

(5) A. I. Vogel, "A Text-Book of Quantitative Inorganic Analysis," 3rd ed, Wiley, New York, N. Y., 1961, pp 259, 363.

(6) T. Chen, *Anal. Chem.*, **39**, 804 (1967).

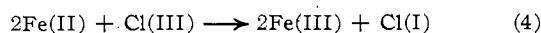
(7) R. M. Milburn and W. C. Vosburgh, *J. Amer. Chem. Soc.*, **77**, 1351 (1955).

(8) R. Bastian, R. Weberling, and F. Palilla, *Anal. Chem.*, **28**, 459 (1956).

(9) D. Leonesi and G. Piantoni, *Ann. Chim.*, **65**, 668 (1965).

(10) W. Buser and H. Hanish, *Helv. Chim. Acta*, **35**, 2547 (1952).

From Table III, the average stoichiometric ratio is 1.98 ± 0.05 . This suggests that the reaction being observed when both phenol and chloride ion are present can be represented as



Reaction Kinetics.—Several preliminary experiments indicated that the reaction deviates from the first-order behavior that would be expected under pseudo-first-order conditions. It is proposed that the observed deviations are due to consecutive reactions of the intermediate product chlorine(I)^{11,12} with either iron(II) or chlorine(III). The typical first-order plot in the absence of initially added chloride ion or phenol deviates from linearity with the slope increasing as the reaction proceeds.

The addition of 0.50 *M* chloride ion to the reaction mixture but no phenol changes the deviation to a decrease in slope with increasing time. This decrease in reaction rate is presumably caused by the rapid conversion of chlorine(I) to chlorine(0) followed by the slow reaction of chlorine(0) with iron(II).

These deviations were completely eliminated when both chloride ion and phenol were present initially in the reaction mixture. Although phenol is a poor scavenger for chlorine(I), it reacts rapidly with chlorine(0) which is produced in the reaction between chlorine(I) and chloride ion. Figure 1 illustrates the

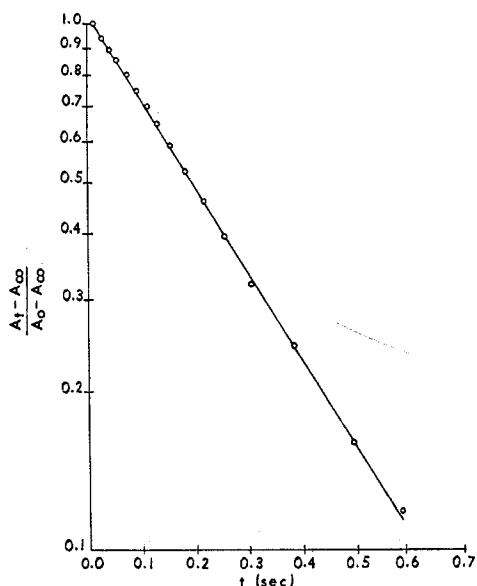


Figure 1.—Pseudo-first-order log plot of the iron(II)-chlorine(III) reaction at 25° with 0.50 *M* chloride ion and 4.22×10^{-4} *M* added. $[\text{Fe(II)}]_0 = 1.92 \times 10^{-3}$ *M*; $[\text{Cl(III)}]_0 = 2.56 \times 10^{-5}$ *M*; $[\text{H}^+] = 0.50$ *M*.

linearity of a pseudo-first-order plot for more than 85% of the reaction in the presence of phenol and chloride ion. It should be pointed out that the presence of phenol in the absence of added chloride ion reduces, but does not completely eliminate, the deviations from linearity. This would be expected in that chlorine(I) reacts only slowly with phenol.¹¹

The observed first-order rate constant was computed

(11) E. B. Grimley, R. J. Buchacek, and G. Gordon, *Inorg. Chem.*, **10**, 873 (1971).

(12) R. J. Buchacek, Ph.D. Thesis, University of Iowa, Iowa City, Iowa, 1972.

by means of a nonlinear least-squares procedure.¹³ The constant is defined according to the following equation such that a direct comparison with the results of Conoccioli, Hamilton, and Sutin¹ is possible

$$\frac{-d[\text{Fe(II)}]}{dt} = \frac{d[\text{Fe(III)}]}{dt} = \frac{-2d[\text{Cl(III)}]}{dt} = k_{\text{obsd}}[\text{Cl(III)}] \quad (5)$$

In view of the 2-equiv stoichiometry which we have established for the reaction, it should be noted that the reaction rate could also be defined in an alternate fashion, such as $-d[\text{Fe(II)}]/2dt$. If the results of the present study are to be compared with other 2-equiv iron(II) reactions in which rate is defined as $-d[\text{Fe(II)}]/2dt$, or if the results are to be compared to a 1-equiv iron(II) reaction, the rate constants reported here must be divided by 2.00.

The order of the reaction with respect to iron(II) was determined by varying the iron(II) concentration over nearly a tenfold change. Although the observed rate is pseudo-first-order in chlorine(III) concentration for about 3 half-lives in each experiment, the initial chlorine(III) concentration was also varied from 1.25×10^{-5} to 4.93×10^{-5} *M*. The apparent second-order rate constant, k'_{obsd} , was determined by dividing k_{obsd} from each experiment by the average iron(II) concentration. At constant hydrogen ion and chloride ion concentrations, the second-order rate constant does not appear to be dependent upon either the initial chlorine(III) concentration or the iron(II) concentration. The results, which are presented in Table IV, are illustrative

TABLE IV
THE EFFECT OF VARYING $[\text{Fe(II)}]_0$ AND $[\text{Cl(III)}]_0$
ON THE OBSERVED SECOND-ORDER RATE CONSTANT AT 10°

$10^5[\text{Cl(III)}]_0$, <i>M</i>	$10^3[\text{Fe(II)}]_0$, <i>M</i>	$10^{-3}k'_{\text{obsd}}$, ^a <i>M</i> ⁻¹ sec ⁻¹	$10^5[\text{Cl(III)}]_0$, <i>M</i>	$10^3[\text{Fe(II)}]_0$, <i>M</i>	$10^{-3}k'_{\text{obsd}}$, ^a <i>M</i> ⁻¹ sec ⁻¹
4.93	0.77	1.09 ± 0.005	2.50	0.77	1.08 ± 0.006
4.93	1.17	1.08 ± 0.004	2.50	6.69	0.96 ± 0.004
4.93	1.84	1.07 ± 0.005	1.25	0.77 ^b	1.32 ± 0.006
4.93	3.68	1.03 ± 0.008	2.50	0.77 ^c	1.37 ± 0.007
4.93	6.69	1.05 ± 0.009	2.50	3.67 ^b	1.40 ± 0.012
2.45	0.77	1.03 ± 0.003	1.25	3.67 ^b	1.44 ± 0.009
2.45	6.69	0.96 ± 0.011			

^a With 0.50 *M* HCl and 7.7×10^{-4} or 2.0×10^{-4} *M* phenol.
^b With 0.05 *M* H⁺ and 0.50 *M* Cl⁻. ^c With 0.04 *M* H⁺ and 0.50 *M* Cl⁻. ^d The uncertainties represent the standard deviations in the fit as computed directly by the computer program.

of the agreement realized between values of the observed second-order rate constant over a wide variety of iron(II) and chlorine(III) concentrations.

The fact that phenol absorbs appreciably at 240 nm made it impractical to vary phenol over a wide concentration range. However, under conditions of excess phenol, the observed second-order rate constant was not affected by a three- to fourfold change in phenol concentration.

The results at both 10 and 25° reflect a decrease in the observed rate constant with increasing hydrogen ion concentration. The slope of a plot of $\log [k'_{\text{obsd}}]$ as a function of $\log [\text{H}^+]$ decreases from -0.07 at high hydrogen ion concentration to -0.22 at 0.05 *M* hydro-

(13) The appropriate values were calculated by means of a computer program in which the square of the differences between the observed and calculated absorbance is minimized. The individual data points were given unit weights. For a description of the algorithm of the computer program, see the Los Alamos publication LA-2367 and addenda.

gen ion concentration. The results of the log-log plot are indicative of a rate law with two parallel pathways in which one of the terms is zero order in hydrogen ion concentration and the other term is dependent upon the inverse of the hydrogen ion concentration. A plot of k'_{obsd} as a function of the reciprocal of the hydrogen ion concentration is shown in Figure 2. This plot is

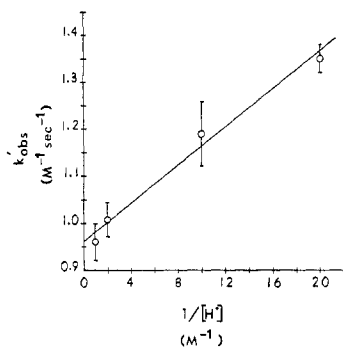


Figure 2. Plot of k'_{obsd} as a function of the reciprocal of the hydrogen ion concentration for the iron(II)-chlorine(III) reaction at 10° .

linear and is consistent with these conclusions. The rate law appropriate to this discussion is given by eq 6.

$$\frac{-d[\text{Fe(II)}]}{dt} = k_1[\text{Fe(II)}][\text{Cl(III)}] + \frac{k_2[\text{Fe(II)}][\text{Cl(III)}]}{[\text{H}^+]} \quad (6)$$

Each data point shown in Figure 2 represents the average rate constant over all chloride ion concentrations studied at that particular hydrogen ion concentration. The error bars correspond to standard deviations as given in Table V. When the k'_{obsd} data are fitted¹⁴ to eq 6 as a function of hydrogen ion concentration, the following rate constants are obtained: $k_1 = (1.89 \pm 0.09) \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$ and $k_2 = 58 \pm 10 \text{ sec}^{-1}$ at 25° ; $k_1 = (0.96 \pm 0.02) \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$ and $k_2 = 20.5 \pm 2.4 \text{ sec}^{-1}$ at 10° . The observed and calculated variations in the apparent second-order rate constant are shown in Table V.

Discussion

Measurements reported here on the iron(II)-chlorine(III) system indicate that the yield of iron(III) dimer in the overall reaction is $\leq 5\%$. The reaction of hydrochlorous acid with iron(II) is known to yield¹ approximately 15% iron(III) dimer. Consequently, some dimer formation is expected as a result of the iron(II)-chlorine(I) interaction which occurs as a side reaction in the absence of a scavenger. Since the acid dissociation constant of hypochlorous acid¹⁵ is 2.90×10^{-8} at 25° , the chlorine(I) predominant species is most likely hypochlorous acid rather than the hypochlorite ion.

Under the conditions at which dimer formation was studied, chlorine(III) and iron(II) react competitively with hypochlorous acid. If it is assumed that 50% of the chlorine(I) intermediate reacts with iron(II) rather than chlorine(III), then 7.5% dimer would be expected from the iron(II)-hypochlorous acid reaction alone. In view of the fact that the total dimer production observed in the present study is even less than 7.5%, it

(14) The nonlinear least-squares program¹³ was used with $1/k'_{\text{obsd}}$ weights in order to minimize the per cent error in the final fit.

(15) J. C. Morris, *J. Phys. Chem.*, **70**, 3798 (1966).

TABLE V
VARIATION OF THE SECOND-ORDER RATE CONSTANT
WITH HYDROGEN ION AND CHLORIDE ION
CONCENTRATIONS AT 2.00 M IONIC STRENGTH

[H ⁺], M	[Cl ⁻], M	$10^{-3}k'_{\text{obsd}}$, $\text{M}^{-1} \text{ sec}^{-1}$	$10^{-3}k_{\text{calcd}}$, $\text{M}^{-1} \text{ sec}^{-1}$
10°			
1.00	1.00	1.00 ± 0.07	
1.00	0.50	0.98 ± 0.06	
1.00	0.10	0.95 ± 0.03	
1.00	0.05	0.91 ± 0.07	
	Av ^a	0.96 ± 0.039	0.98
0.50	1.00	1.03 ± 0.04	
0.50	0.50	1.05 ± 0.05	
0.50	0.10	0.96 ± 0.01	
0.50	0.05	0.99 ± 0.01	
	Av ^a	1.008 ± 0.040	1.00
0.10	1.00	1.21 ± 0.04	
0.10	0.50	1.27 ± 0.06	
0.10	0.10	1.10 ± 0.08	
	Av ^a	1.193 ± 0.086	1.16
0.05	1.00	1.34 ± 0.01	
0.05	0.50	1.38 ± 0.04	
0.05	0.10	1.32 ± 0.01	
	Av ^a	1.347 ± 0.031	1.37
25°			
1.00	0.50	1.91 ± 0.08	1.94
0.50	0.50	1.97 ± 0.07	2.00
0.13	0.50	2.58 ± 0.10	2.34
0.10	0.50	2.33 ± 0.06	2.47
0.08	0.50	2.78 ± 0.04	2.62
0.05	0.50	2.95 ± 0.22	3.06

^a The uncertainties represent standard deviations from the average at constant chloride ion concentration.

appears likely that essentially no dimeric iron(III) is formed during the reduction of chlorine(III) itself. Probably the most important implications of these observations are that the iron(II)-chlorine(III) reaction yields no iron(IV) as an intermediate product and the reaction whose overall stoichiometry is given by eq 4 must involve two successive one-electron-transfer steps.

The hydrogen ion dependence in the iron(II)-chlorine(III) reaction reflects two parallel reaction paths. The hydrogen ion independent term corresponds to an activated complex of the composition $[\text{FeClO}_2\text{H}]^{2+}$. Since the predominant species in highly acid solution are Fe^{2+} and HClO_2 , k_1 is most likely the bimolecular rate constant for the reaction of aquated iron(II) with chlorous acid. The rate constant, k_2 , in the hydrogen ion dependent term is probably the product of a hydrolysis constant and a second-order rate constant

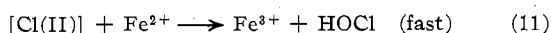
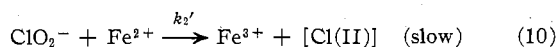
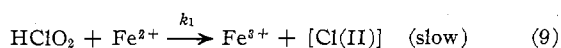
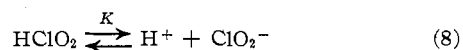
$$k_2 = k_2'K \quad (7)$$

Although the hydrolysis constant may represent a number of processes, most likely it is either the acid dissociation constant for chlorous acid or the formation constant for FeOH^+ . At 25° and 1.0 M ionic strength the first hydrolysis constant¹⁶ for iron(II) is 3.2×10^{-10} . With this value and the experimental result for k_2 of 58 sec^{-1} , the calculated value of k_2' is $1.8 \times 10^{11} \text{ M}^{-1} \text{ sec}^{-1}$. In general, the bimolecular rate constant for a diffusion-controlled process is on the order of 10^9 - $10^{10} \text{ M}^{-1} \text{ sec}^{-1}$. Consequently, a second-order rate constant of $1.8 \times 10^{11} \text{ M}^{-1} \text{ sec}^{-1}$ is unreasonable

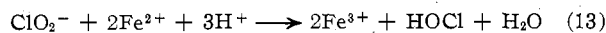
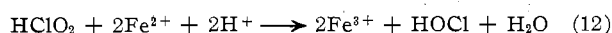
(16) B. O. A. Hedstrom, *Ark. Kemi*, **5**, 457 (1953).

because it implies that the reaction between FeOH^+ and chlorous acid is faster than the diffusion-controlled process. A more reasonable value of k_2' is obtained if the acid dissociation constant for chlorous acid is used. Although K_a for chlorous acid is likely to vary with change in temperature and ionic strength, the approximate value is 0.01.^{9,17} At 10°, k_2 has been measured to be 20 sec^{-1} , and at 25° it is 58 sec^{-1} . With a value of 0.01 for K , the calculated values of k_2' at 10 and 25° are 2.0×10^3 and $5.8 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$, respectively.

These values of k_2' , obtained by assuming that the hydrogen ion dependence is due to chlorous acid dissociation, are quite reasonable. Mechanistically, k_2' corresponds to the second-order rate constant for the reaction between iron(II) and chlorite ion. A reasonable mechanism consistent with this interpretation is



Since it is difficult to predict the composition of the chlorine(II) intermediate in the above mechanism, the role of hydrogen ions and water molecules is not specified. However, these species are included in the balanced equation for the overall reaction stoichiometry according to either of the equivalent expressions



The rate of oxidation of iron(II) by chlorine(III) was not studied in the absence of added chloride ion, but kinetic results were obtained over a wide range of chloride ion concentrations. The chloride ion dependence is comparable to that observed in the iron(II)-hydrogen peroxide reaction^{18,19} in that the rate increases only slightly with increasing chloride ion concentration. The overall effect of chloride ion is similar

to that observed by Po and Sutin.²⁰ When chloride ion is varied from 0.1 to 1.0 M , at constant hydrogen ion concentration, k'_{obsd} increases less than 7%. Over the range of 0.1–1.0 M chloride ion, Po and Sutin measured a rate increase of about 9%. However, Wells and Salam^{18–20} reported a 25% increase in rate over essentially the same concentration range. Thus, the results reported here at 10° and 2.0 M ionic strength are consistent with the conclusions of Po and Sutin that the stability constant of FeCl^+ must be less than 0.5 M^{-1} .

It is of additional interest to compare several 2-equiv reactions where the reductant is either iron(II) or $\text{Fe}(\text{phen})_3^{2+}$. Chlorine(I) reacts with $\text{Fe}(\text{phen})_3^{2+}$ by both one- and two-electron steps. In our previous report on the $\text{Fe}(\text{phen})_3^{2+}$ system,² it was possible to vary the conditions such that either the one-electron path or the two-electron path would predominate. Chlorine(I) also appears to react with aquated iron(II) by parallel one- and two-electron steps.¹

Under specific conditions, chlorine(I), chlorine(III), and hydrogen peroxide all react with the iron-phenanthroline complex *via* primarily a two-electron pathway. However, it is noteworthy that of the three oxidants just mentioned, chlorine(I) is the only one which exhibits any evidence of two-electron transfer with aquated iron(II). Evidently coordinated phenanthroline inhibits the outer-sphere one-electron oxidation process. It is also possible that in the bis(1,10-phenanthroline) complex, the 4+ oxidation state of iron is thermodynamically stabilized such that a two-electron oxidation is facilitated.

In light of the results of the present study, it is becoming increasingly evident that two-electron transfer must be preceded by substitution of the oxidant into the inner coordination sphere of the metal ion. Although one-electron redox reactions may be inner-sphere or outer-sphere reactions, the evidence is compelling that two-electron processes must be inner-sphere reactions.

Acknowledgments.—The authors are grateful to the Atomic Energy Commission for support under Contract At-(11-1)-1780.

(20) H. N. Po and N. Sutin, *Inorg. Chem.*, **7**, 621 (1968).

(17) R. Tachiki, *J. Chem. Soc. Jap.*, **65**, 346 (1944).

(18) C. F. Wells, and M. A. Salam, *Trans. Faraday Soc.*, **63**, 620 (1967).

(19) C. F. Wells, *J. Chem. Soc. A*, 2471 (1969).